Total Ammonia and Un-ionized Ammonia Concentrations in the Delta

An examination of ambient concentrations and toxicity thresholds

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Presented at the Central Valley Regional Water Quality Control Board's

Ammonia Summit

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Sacramento, CA

LARRY WALKER ASSOCIATES

Outline

Data/Stations

- Sources of Data
- Classification of Stations as Estuarine or Freshwater
- Geographic Distribution of Data

Screening of Ambient Data for Total Ammonia

- Using Current EPA Chronic and Acute Criteria
- Using a Hypothetical Doubly Strict Acute Criterion

Ambient Un-ionized Ammonia Concentrations

- Ranked Distributions of Ambient Data
- Comparisons to Experimental Toxic Effects Thresholds

Conclusions

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Sources of Data

All available surface grab samples with values for:

- total (or dissolved) ammonia
- pH
- water temperature, and
- salinity or electrical conductivity

Entities:

- IEP-EMP
- USGS
- DWR-MWQI
- SRCSD-CMP

Stations:

55 stations in the legal Delta, and Suisun and San Pablo Bays

Timeframe: 1974-2009

The dataset consisted of 10,543 grab samples

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Salinity of water samples potentially affects:

1. **How un-ionized ammonia (f_{NH3}) should be calculated**

2. **Decision rules for exceedances of EPA criteria**

How so?….

Un-ionized Ammonia Fraction (f_{NH3}) is calculated differently in…

Saltwater:

$$f_{NH_3} = \frac{1}{1+10^{\left[pK_a + 0.0324(298-T) + \frac{(0.0415)P}{T} - pH\right]}}$$

$$pK_a = 9.245 + 0.116 \times I$$

$$I = \frac{19.9273 * S}{(1000 - 1.005109) * S}$$

(where S = salinity)

Freshwater:

$$f_{NH_3} = \frac{1}{1+10^{pK-pH}}$$

$$pK = 0.09018 + \frac{2729.92}{273.2 + T}$$

and EPA Ammonia Criteria are calculated differently in saltwater and freshwater…

Saltwater **Acute Criterion**

$$C_{CMC} = \frac{0.233}{f_{NH_3}}$$

Freshwater **Acute Criterion**

(salmonids present)

$$C_{CMC} = \frac{0.275}{1 + 10^{7.204 - pH}} + \frac{39.0}{1 + 10^{pH - 7.204}}$$

Saltwater Chronic Criterion (CCC)

$$C_{CCC} = \frac{0.035}{f_{NH_3}}$$

Freshwater Chronic Criterion (CCC)

(early life stages present)

$$C_{CCC} = \left(\frac{0.0577}{1+10^{7.688-pH}} + \frac{2.487}{1+10^{pH-7.688}} \right) \times MIN\left(2.85, 1.45 \times 10^{0.028 \times (25-T)}\right)$$

When should freshwater and saltwater ammonia criteria apply in estuaries?

The California Toxics Rule (which applies to 126 metals and organic compounds) provides potential guidance.

California Toxics Rule (CTR) states:

- **Freshwater Criteria** apply at a site when Salinity ≤ 1 ppt 95% or more of the time
- **Saltwater Criteria** apply at a site when Salinity ≥ 10 ppt 95% or more of the time
- Otherwise, **the more stringent of the criteria apply** (i.e., you should calculate both saltwater and freshwater criteria for each sample)

Stations were classified as Freshwater, Saltwater, or Estuarine using the approach in the CTR

- **some stations had Salinity data (ppt)**
- **some stations had EC data (µS/cm)**

If ≥ 95% of samples in the record had..	Site was classifed as…
Salinity ≤ 1 ppt (or EC ≤ 2,100)	Freshwater
Salinity ≥ 10 ppt (or EC ≥ 18,750)	Saltwater
Otherwise,…	Estuarine

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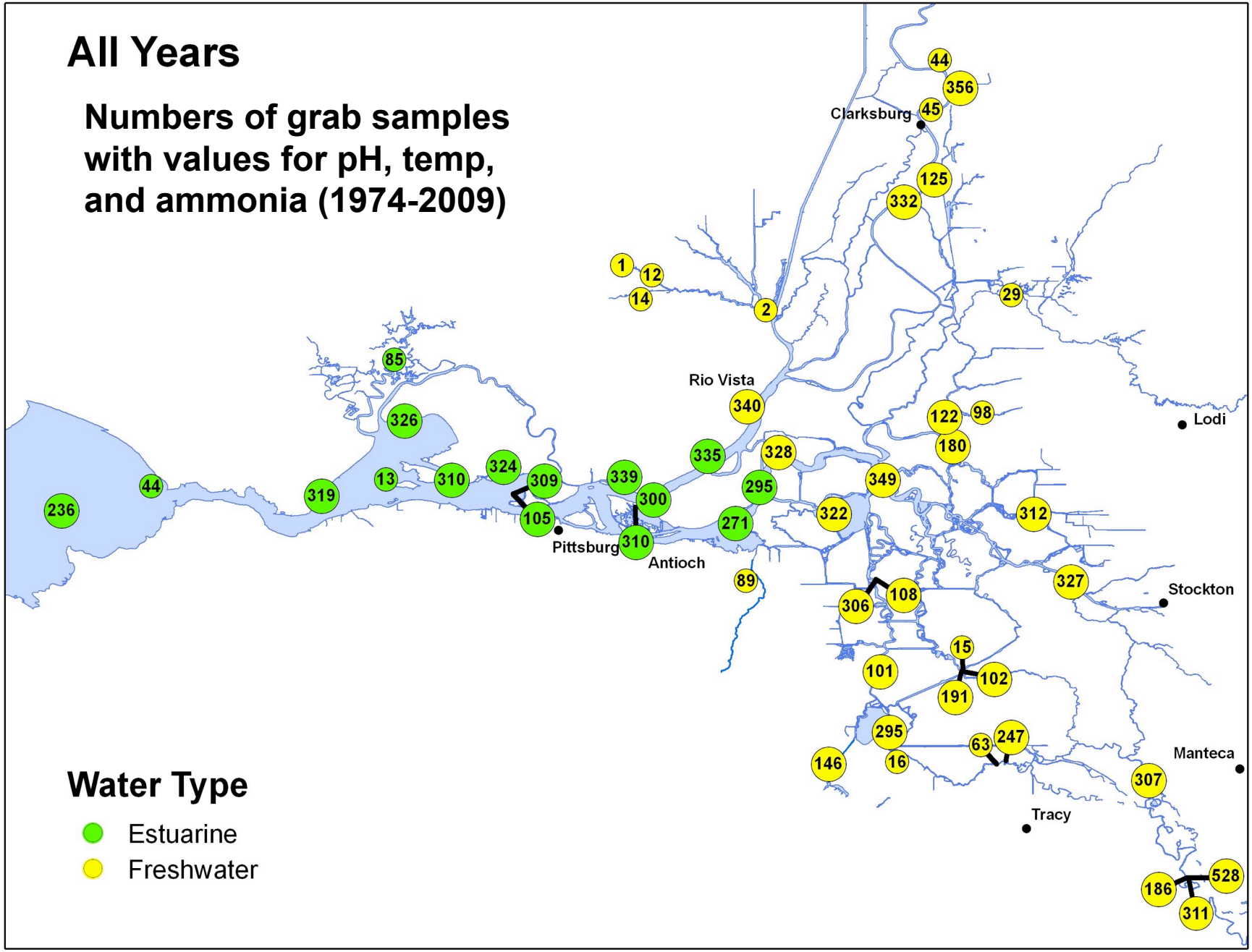

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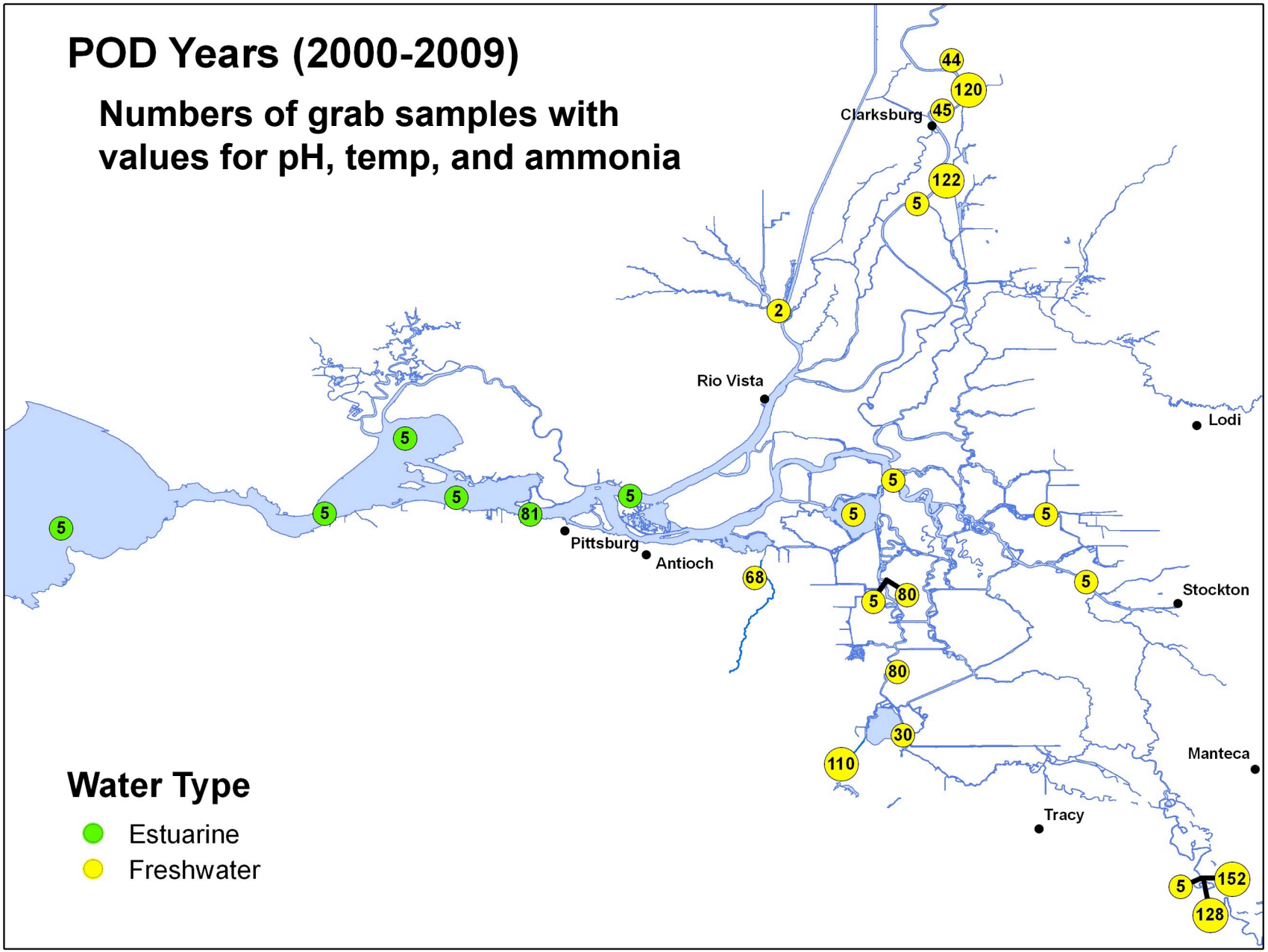

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Screening Ammonia Data using Current EPA Criteria

Freshwater Stations:

Ambient Total (or Dissolved) Ammonia (mg N/L) compared to:

- ***Freshwater CMC***
- ***Freshwater CCC***

Screening Ammonia Data using Current EPA Criteria

Estuarine Stations:

***Whichever CMC and CCC was stricter** (saltwater or freshwater) for each sample was compared to ambient total (or dissolved) ammonia (mg N/L).*

The saltwater criteria require computation of f_{NH3}. f_{NH3} was obtained 2 ways, resulting in two separate screenings:

1. consider salinity of individual samples

f_{NH3} calculated using saltwater formula for brackish samples (EC > 2,100)

2. more conservative

f_{NH3} calculated for all samples using freshwater formula

Collectively, over half of the samples from estuarine sites were brackish

$$\frac{2302}{4016}$$

How often was the saltwater criterion more stringent than the freshwater criterion for samples from estuarine stations?

The Freshwater Acute Criterion was stricter than the Saltwater Acute Criterion in almost 90% of the samples from estuarine sites.

This result varied little depending on whether f_{NH3} in brackish samples was calculated using the freshwater or saltwater formula.

	percentage of samples for which the stricter Acute Criterion was the…	
Method for Calculating the Un-ionized Ammonia Fraction	***Freshwater CMC***	***Saltwater CMC***
Use f_{NH3}-salt for brackish samples	89%	11%
Use f_{NH3}-fresh for brackish samples	88%	12%

But, the Saltwater Chronic Criterion was stricter than the Freshwater Chronic Criterion in 80% of the samples from estuarine sites.

Again, this result varied little depending on whether f_{NH3} in brackish samples was calculated using the freshwater or saltwater formula.

	percentage of samples for which the stricter Chronic Criterion was the…	
Method for Calculating the Un-ionized Ammonia Fraction	***Freshwater CCC***	***Saltwater CCC***
Use f_{NH3}-salt for brackish samples	20%	80%
Use f_{NH3}-fresh for brackish samples	19%	81%

Results for Estuarine Stations

Out of 4018 monthly grab samples,

0 exceedances of EPA criteria

(of either CMC or CCC)

For a sample size of 4018, State Listing Policy Procedures (for Toxicants) would require 345 exceedances to trigger a 303(d) listing.

Results for Freshwater Stations

Out of

6,525 monthly grab samples

only 2 exceedances (of CCC)

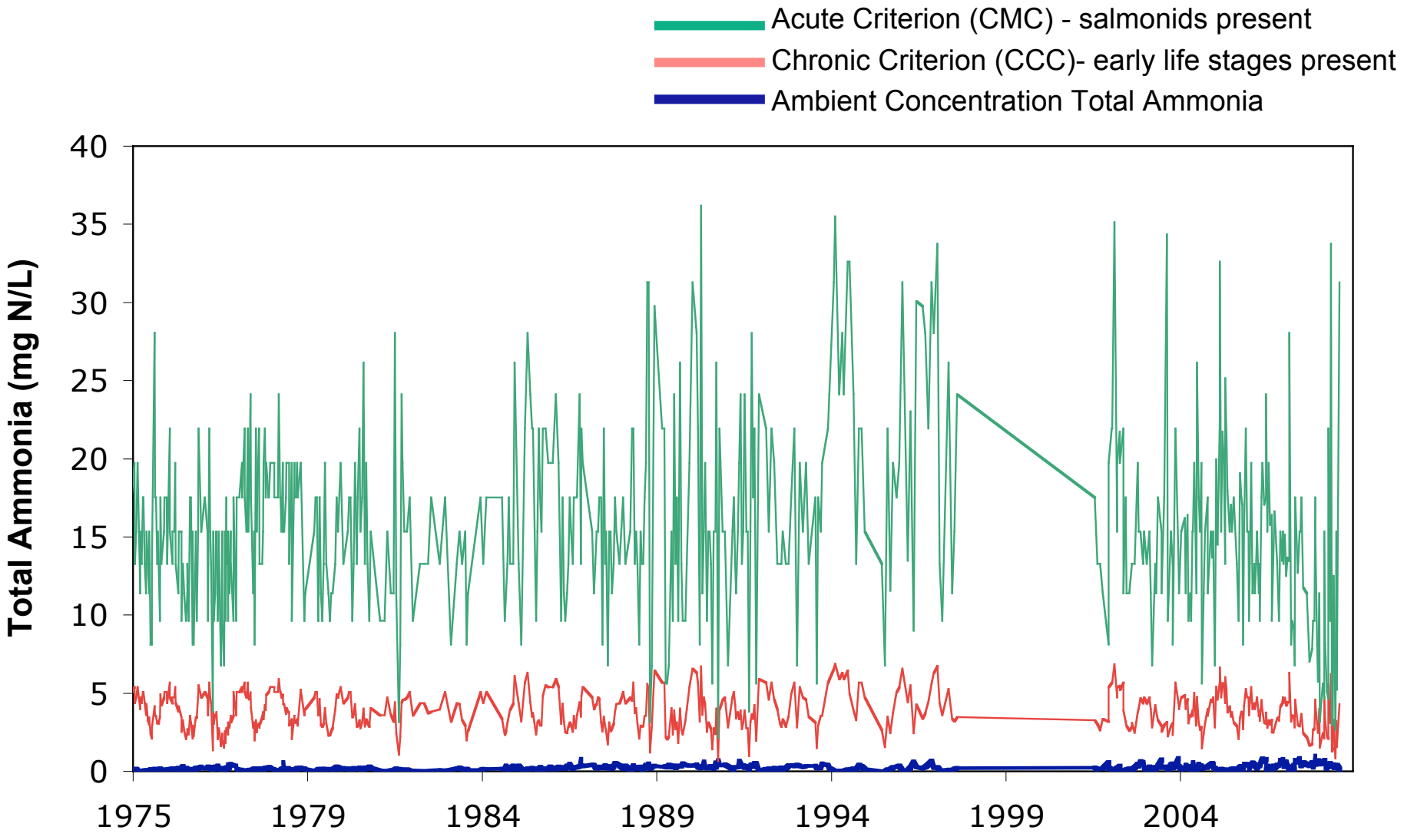
- **Normally, EPA chronic criteria would apply to 4-day (saltwater) or 30-day* (freshwater) averaging periods, not to monthly grabs.**

- ***For a sample size of 6525, State Listing Policy Procedures (for Toxicants) would require 560 exceedances to trigger a 303(d) listing.***

**provided the highest 4-day average is not greater than 2 x CCC.*

Upper Sacramento River

Sacramento River @ Hood (DWR-MWQI)
Sacramento River @ Greenes Landing (USGS, IEP, DWR-MWQI)
River Mile 44 (SRCSD-CMP)



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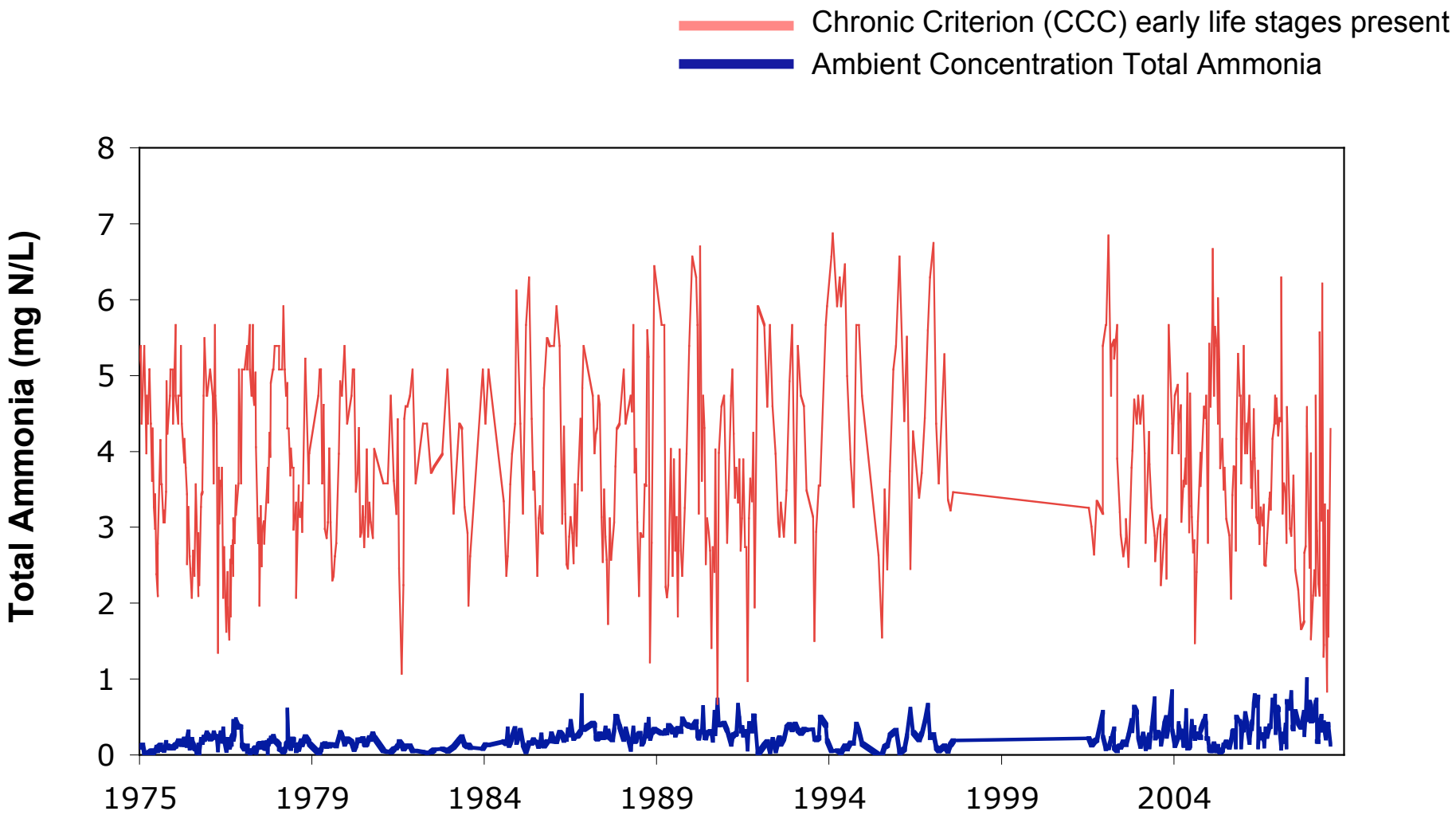

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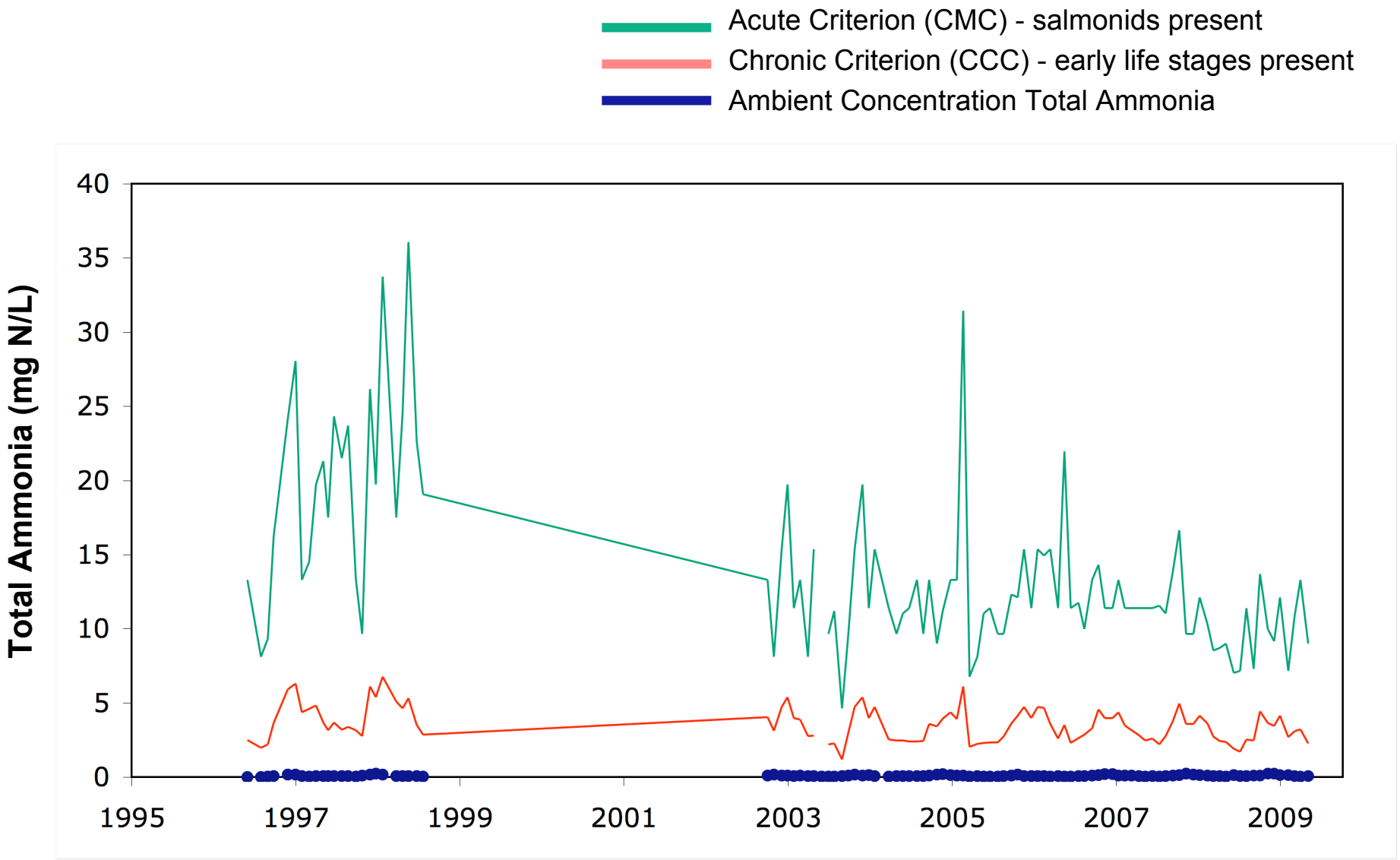
Sacramento River - mouth

Sacramento River @ Mallard Island (DWR-MWQI E0B80261551)



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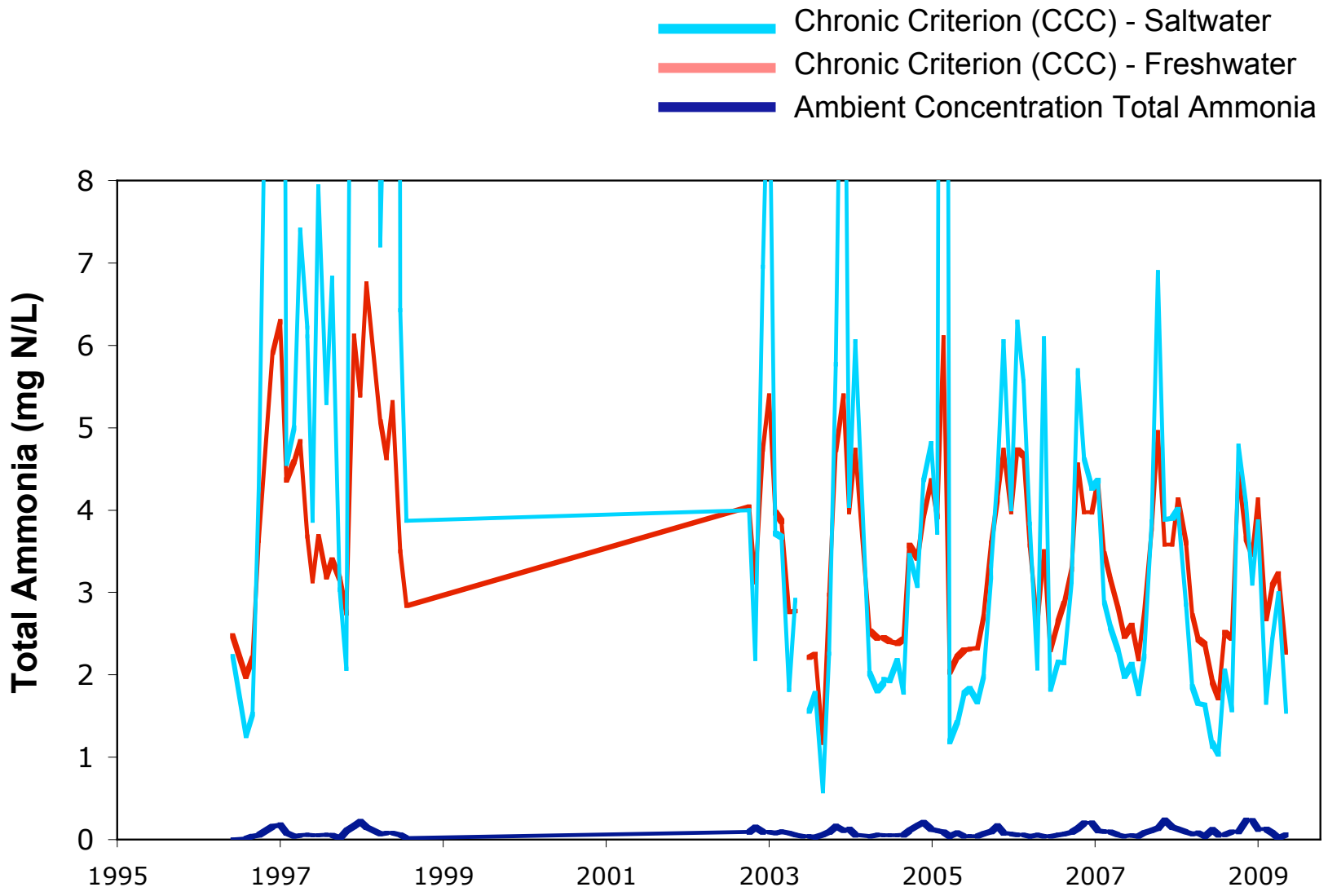

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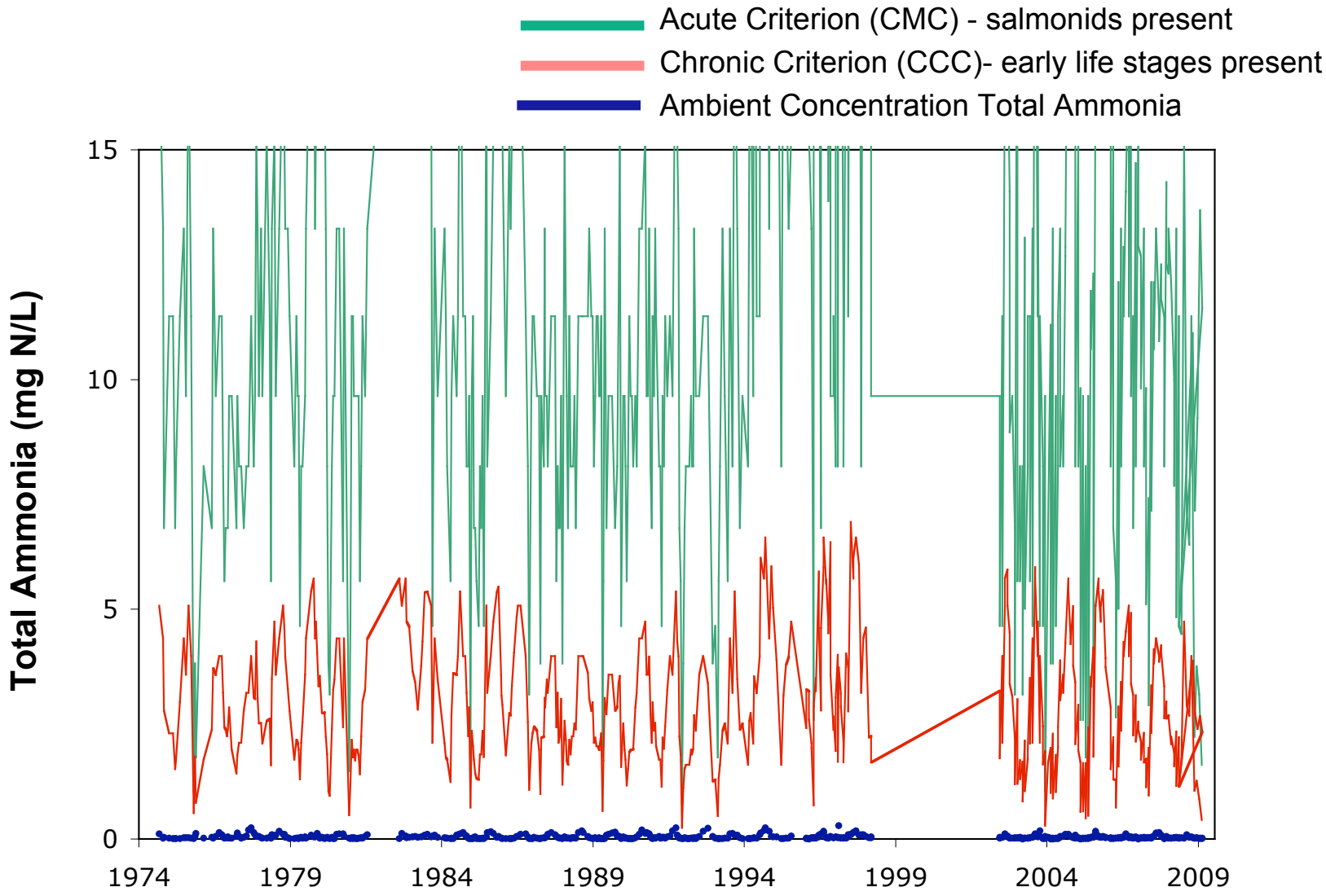
Old River (between Frank's Tract and CCF)

Old River @ Bacon Island (DWR-MWQI B0D75811344)
Old River @ Rancho del Rio (IEP-EMP D28A)
Old River nr. Byron (DWR-MWQI B9D75351342)



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Are EPA criteria sufficiently protective?

What if a Delta fish or invertebrate was more (acutely) sensitive to un-ionized ammonia than the most sensitive organism* used in the 1999 freshwater EPA database?

*rainbow trout

The 1999 EPA Freshwater CMC was calculated by…

using the SMAV for rainbow trout in place of the "5th percentile of ranked GMAVs" as follows:

1. Take the SMAV for rainbow trout (11.23 mg N/L)
2. Divide by 2 (5.615)
3. Use result in equation below

5.615

$$CMC = (AV_{t,8})\left(\frac{0.0489}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}}\right)$$

$$CMC = \frac{0.275}{1+10^{7.204-pH}} + \frac{39.0}{1+10^{pH-7.204}}$$

Now, use a value for a hypothetical fish/invertebrate twice as sensitive as rainbow trout…

1. Take a hypothetical SMAV one-half that of rainbow trout (5.5 mg N/L)
2. Divide by 2 (2.75)
3. Use result in equation below

$$CMC = (AV_{t,8})\left(\frac{0.0489}{1+10^{7.204-pH}} + \frac{6.95}{1+10^{pH-7.204}}\right)$$

New Formula: $$CMC = \frac{0.134}{1+10^{7.204-pH}} + \frac{19.1}{1+10^{pH-7.204}}$$

Results using Hypothetical Doubly-Strict CMC

Estuarine stations:
0 exceedances in 4018 monthly grab samples

Freshwater stations:
1 exceedance in 6,525 monthly grab samples

(San Joaquin River nr. Vernalis, 1992)

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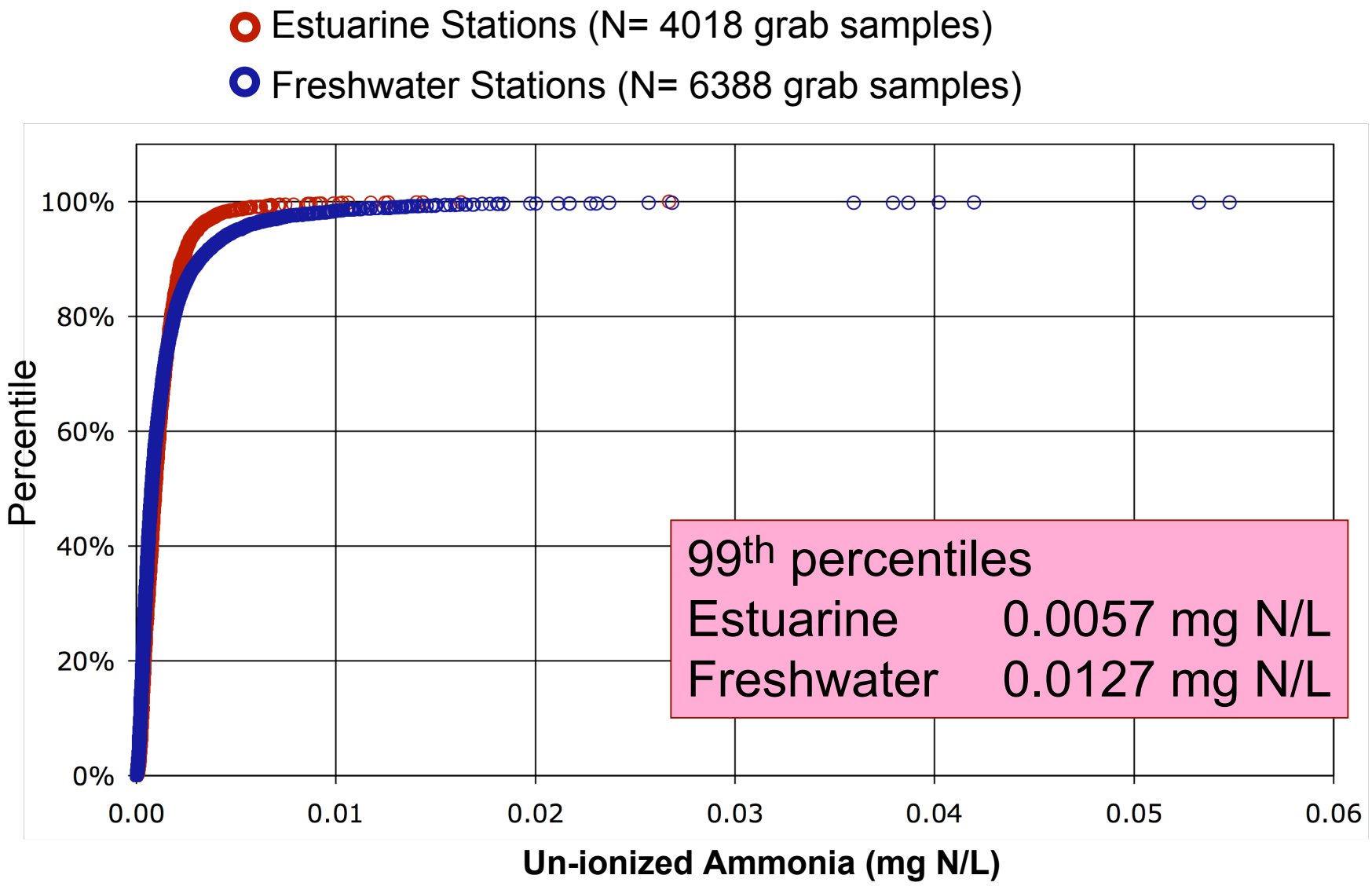
Ranked Distribution of Un-ionized Ammonia Concentrations (1975-2009)



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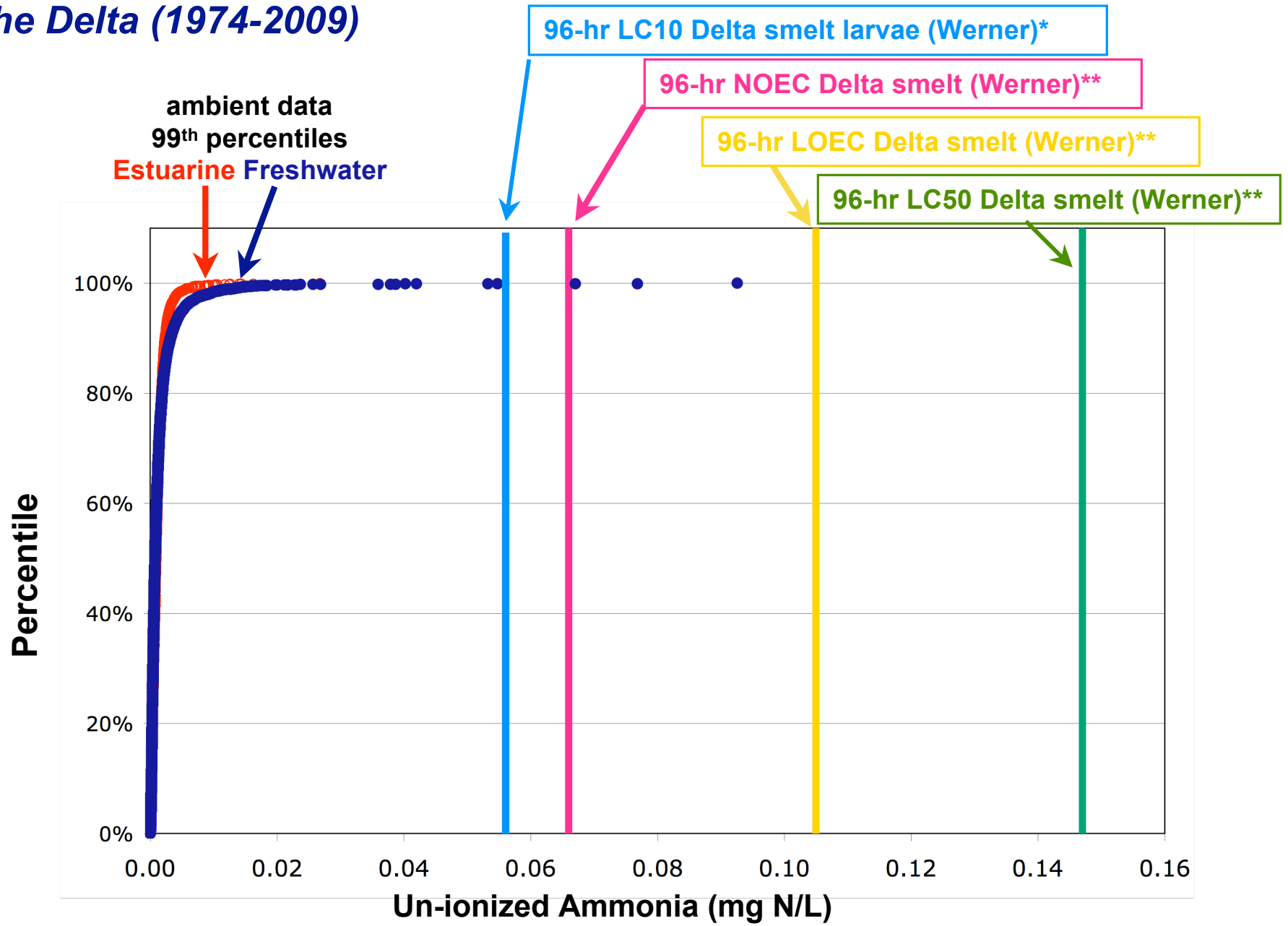
Cumulative Distribution of Un-ionized Ammonia Concentrations in the Delta (1974-2009)



*I. Werner, pers. comm., 8/28/09
**S. Fong, pers. comm., 8/06/09

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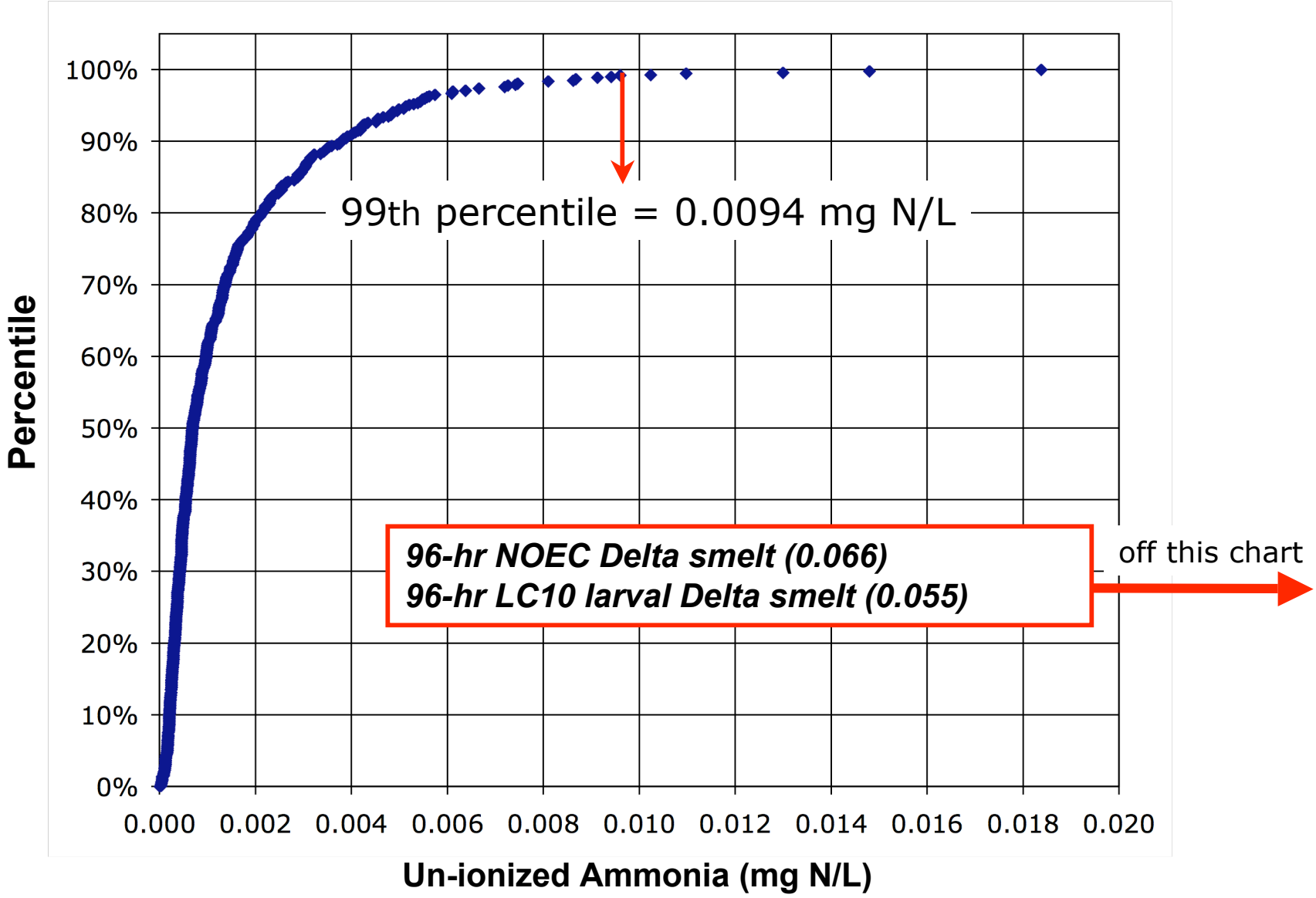
Ranked distribution of un-ionized ammonia for freshwater stations, POD years only (2000-2009)



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Conclusions

A. Use of Saltwater vs Freshwater Criteria

- ***Using the salinity thresholds in the CTR, 15 stations (including some in the legal Delta) would be classified as Estuarine***
- ***At estuarine stations, the Freshwater Acute Criterion was usually stricter than the Saltwater version (89% of samples),***
- ***but the Saltwater Chronic Criterion was usually stricter than the Freshwater version (80% of all samples)***

Conclusions

B. Screening of Ambient Total Ammonia data

- *10,543 grab samples from 55 monitoring stations were screened for exceedances of applicable EPA acute and chronic criteria for total ammonia.*

- *Only 2 exceedances (of the chronic criterion), and no exceedances of the acute criterion, were observed in this dataset using current EPA criteria.*

- *Recalculating the EPA acute criterion to account for a species twice as sensitive as rainbow trout resulted in only 1 exceedance in this dataset.*

Conclusions

C. Un-ionized Ammonia Concentrations

- *The 99th percentile values for un-ionized ammonia concentrations (using all data) were:*
  - *0.0057 mg N/L (Estuarine stations)*
  - *0.0127 mg N/L (Freshwater stations)*
- *The 99th percentile value for POD years at freshwater sites was 0.0094 mg N/L*
- *Only 3 samples (out of 10,406) had concentrations of un-ionized ammonia that exceeded effects thresholds provided for Delta smelt.*
- *California State Listing Policy for toxicants would require a minimum of 538 exceedances to trigger a 303(d) listing for a sample size as large as this one from the Freshwater Delta.*